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STEAM PRETREATMENT FOR COAL LIQUEFACTION

Third Quarterly Report

For the Period

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ABSTRACT

Steam pretreatment is the reaction of coal with steam at temperatures well below those usually used for solubilization. The objective of the proposed work is to test the application of steam pretreatment to coal liquefaction. A 300 ml stirred autoclave for liquefaction tests is being installed. A nonflow steam pretreatment procedure has been established for work with model compounds. Pretreatment tests with Blind Canyon coal, a coal similar to Illinois No. 6 but containing no sulfur, have been started. These initial tests show only a slight increase in yield resulting from pretreatment. A method for purifying α -naphthylmethyl phenyl ether has been found which avoids its acid catalyzed rearrangement. Alpha-benzyl-naphthyl ether has been pretreated and the products tentatively identified.

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INTRODUCTION

This is the third quarterly report of a two year program on the application of steam pretreatment to the direct liquefaction of coal. Steam pretreatment is the reaction of coal with steam at temperatures well below those usually used for solubilization.

Steam pretreatment has been shown to be effective in coal pyrolysis. For steam pyrolysis, it has more than doubled the liquid yield, reduced the molecular weight of pyrolysis liquid by 31%, and increased yields in mild extraction. Studies of pretreated Illinois No. 6 coal indicate that steam reacts with the ether linkages in coal, replacing them with hydroxyl groups. The result is a partially depolymerized coal. The oxygen content of this pretreated coal is 27% that of the feed.

These results suggest that steam pretreatment prior to solubilization will be beneficial to the coal liquefaction process. It is the objective of this work to test this application. Direct liquefaction of steam pretreated coals will be carried out in a stirred autoclave and the results compared with those from the liquefaction of raw coal.

It is also an objective of this work to develop an improved understanding of the chemistry of steam pretreatment. For this purpose, model compounds will be reacted with steam under the same conditions as used for coal pretreatment and their products analyzed to determine reaction pathways.

CONSTRUCTION OF LIQUEFACTION TEST APPARATUS

Installation of the 300 ml stirred autoclave to be used in direct liquefaction tests was continued this quarter. Special tools required for equipment operation have been acquired. To avoid serious delays for equipment maintenance, a selection of spare parts has been obtained from the manufacturer. Assembly will be continued next quarter.

PRETREATMENT STUDIES

The yield of volatiles released during pretreatment of Illinois No. 6 coal was determined to be 8.3 % (based on maf raw coal) at 340 C and 750 psia using the continuous flow system.

Nonflow Procedure

For work with model compounds, some type of nonflow system is needed to avoid loss of the starting material or its volatile products. In order to verify the nonflow method, it was first tested with coal using extraction yield as the indicator of pretreatment.

The first type of system tested consisted of a stainless steel tube loaded with coal and water and sealed with compression fittings and valves at each end. The required amount of water was calculated in each case to be that needed to give a pressure of 750 psia in the reactor volume when fully vaporized at the pretreatment temperature. The results for five tests are given in Table 1 (based on maf raw coal, volatiles loss not included). These yields, rather than being higher than raw coal, are only half that value for which the average of three runs is 13.7% (Table 1, Second Quarterly Report, 1 January to 31 March 1991).

Table 1
Nonflow Pretreatment of Illinois No. 6 Coal (CFI 27A)

Run No.	Reactor Volume (ml)	Amount of Water (ml)	Temperature (C)	Extraction Yield (%)
B1	11	0.176	320	5.6
B2	15	0.230	320	6.0
B3	15	0.300	340	5.3
B4	14	0.300	340	6.61
B5	15	0.000	340	5.94

Since the same yields are obtained with and without (run B5) water, these results suggest that an inadequate pressure of water was maintained in the bomb. Leakage is one possible explanation. Absorption of water by coal is another. Pretreated coal swells in

water by a factor of 2. Hence, the 3 gram samples used here could imbibe ten times the quantity of water added. To directly measure the pressure during pretreatment, a tubing bomb with extension tube for pressure measurement was tested. The tubing bomb construction was as described by P.S. Maa, R.C. Neavel and L.W. Vernon, 1984. The tubing bomb was charged with water to check the pressure reading, but the method proved infeasible because of water condensation in the extension tube.

To overcome these difficulties, the system was changed to nonflow, open operation. In this arrangement, the reactor outlet valve is kept closed but the reactor is continuously supplied with steam at 750 psia (as previously described for continuous flow operation). This procedure gave satisfactory results. In a pretreatment test at 350 C and 750 psia, an extraction yield of 25.0% (maf raw coal, volatiles not included) which agrees with the results obtained last quarter in continuous flow operation. Therefore, this procedure can now be used with confidence for the processing of model compounds (vide infra).

Blind Canyon Coal

A new coal sample, Penn State Sample Bank DECS-6, Blind Canyon, has been obtained. This coal is of the same rank as Illinois No. 6 coal, has a closely similar maceral content but is almost totally without iron and sulfur. Consequently, it is an excellent choice for testing the importance of these elements in pretreatment.

Pretreatment tests of Blind Canyon Coal were initiated. The sample was used as received with a particle size of -20 mesh. Its moisture content was determined to be 4.23%. Two pretreatment tests were made at 335 and 340 C, operating with a continuous flow of steam. Extraction yields for raw and pretreated coal are given in Table 2 based on the daf raw charge; volatiles losses are not included.

Table 2
Continuous Flow Pretreatment of Blind Canyon Coal.

Run No.	Temperature (C)	Pressure (psi)	Extraction Yield (%)
RBE 1	raw	-	13.08
RBE 2	raw	-	13.79
FBE 2	335	750	14.74
FBE 1	340	750	15.62

Evidently, Blind Canyon coal shows only a very slight response to steam pretreatment (under similar conditions, the extraction yield for Illinois No. 6 coal increased from 14% to 25%). The yield of volatiles during steam pretreatment of Blind Canyon coal is also low. It was determined to be 4.1% at 335 C, 750 psi and 4.35% at 340 C, 750 psi. This is about half the corresponding value for Illinois No. 6 coal.

Pretreatment studies of Blind Canyon coal will be continued next quarter. Pretreatment runs at higher and lower temperatures will be made. To test for catalytic components present in Illinois No. 6 coal but not in Blind Canyon coal, mixtures of the two coals will be pretreated.

MODEL COMPOUND STUDIES

Model Compound Purification

The acid catalyzed rearrangement product of α -naphthylmethyl phenyl ether (α -NMPE) was further examined this quarter. Separation was accomplished by HPLC using hexane (Silica-25 X 0.4 cm-1.0 ml/min). The resolution index ($R_s = t_1 t_2 / 2(t_1 + t_2)$) for the procedure is estimated to be 1.0 (Figure 1).

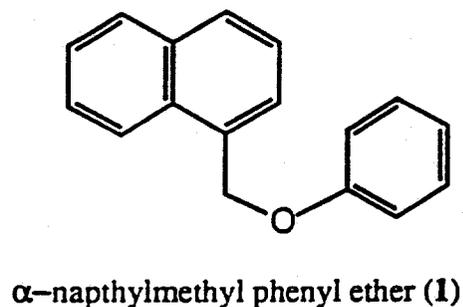
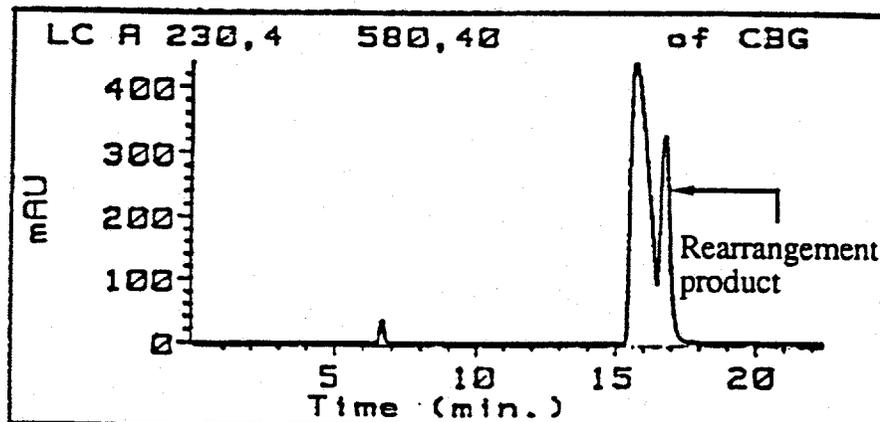


Figure 1. HPLC profile of mixture with R_s of 1.0.

Although the HPLC trace for the separated rearrangement product (Figure 2, left) appears to be that of a pure substance, closer examination reveals the possible presence of more than one component. Confirmation of this is obtained by examining the variation of absorbance with elution time at two wavelengths. The HPLC trace was monitored at 254 nm (upper plot, Figure 2, right) and 258 nm. The ratio of the absorbance at these two wavelengths (lower plot, Figure 2, right) is not flat (as it would be for a pure compound), demonstrating the presence of more than one component.

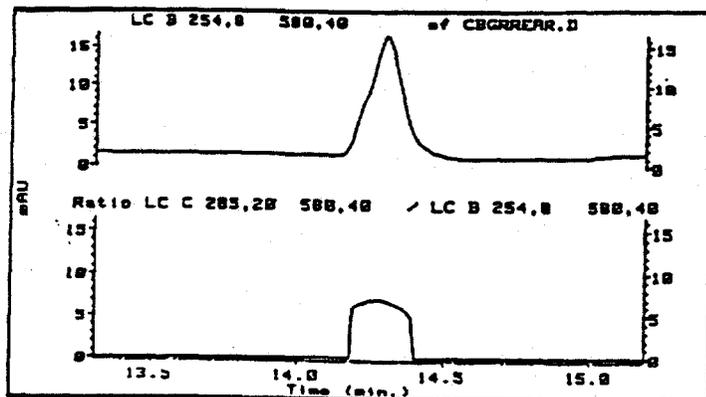
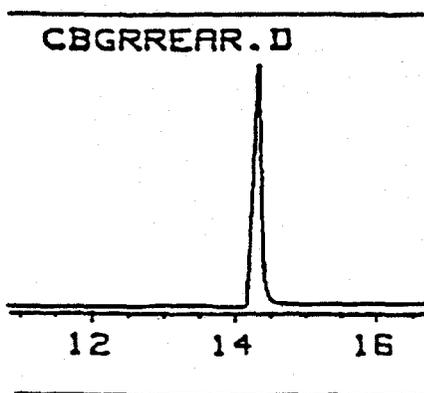


Figure 2. HPLC and ratio plots of rearrangement products.

Development of isolation procedures and separation methods to correctly identify the rearrangement products will aid in the elucidation of the mechanisms pertinent to their production in coal liquefaction.

Flash column chromatography using alumina improved purification of α -NMPE. A purity of 99.48% was obtained from one chromatographic run, up from 95% (Figure 3.). Purification of α -NMPE is continuing.

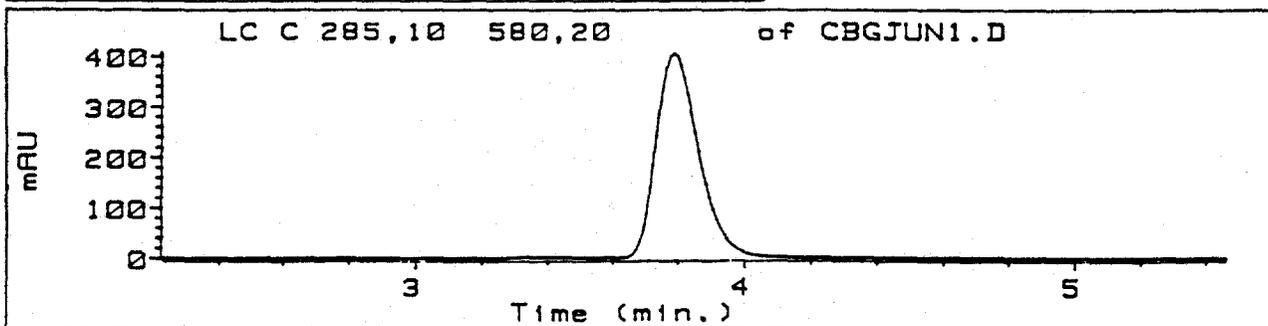
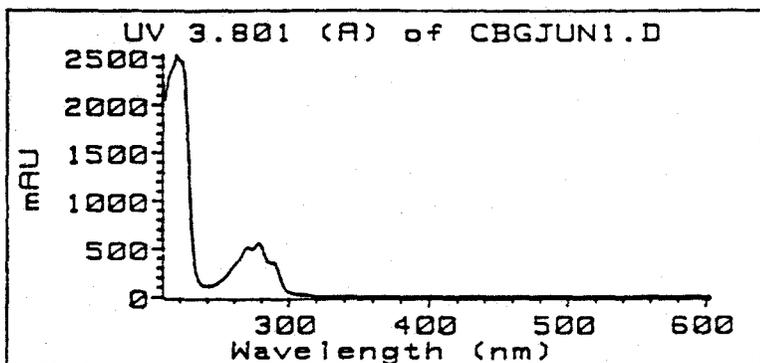


Figure 3. HPLC Profile of α -naphthylmethyl phenyl ether purified with flash column chromatography on alumina.

Steam Pretreatment of Model Compounds

Two pretreatment tests have been conducted with model compounds using the non-flow procedure described above month. In the first test, 300 mg of α -benzyl-naphthyl ether (α -BNE) was treated with steam for 15 minutes at 319 C and 750 psia (run MK1-1).

After pretreatment, the gas phase present in the reactor tube was analyzed by mass spectrometer. This showed that carbon monoxide and toluene were formed during the pretreatment procedure.

Washing the residue in the reactor with methylene chloride produced 205 mg of extractable material. Proton NMR analysis of this methylene chloride soluble material showed none of the starting material (Figure 4).

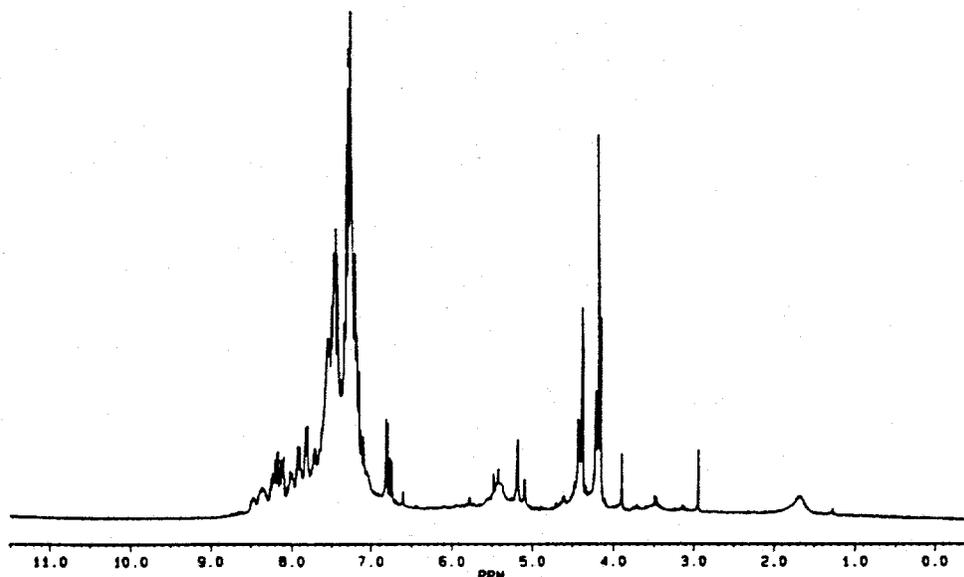


Figure 4. ^1H NMR (in CDCl_3) of methylene chloride extract showing the absence of starting material (α -BNE).

This extract was also analyzed by GS-MS. Chemical ionization using ammonia showed six significant components with molecular masses 144, 180, 218, 234, 234 and 324. Analysis of these chemical ionization (CI) and electron ionization (EI) profiles, combined with MS library analysis and previously reported studies, has allowed us to assign structures based solely on the mass spectral data (Figure 5). These assignments are tentative. The additional use of other methods of spectroscopic analysis will allow us to more positively establish the structures of these compounds.

Chromatographic analysis (preparative TLC on alumina) was also performed to separate the components of the methylene chloride extract. A hexane/ether combination was sufficient to separate the extract into seven bands (Figure 6). Band 1 on GC-MS analysis

showed the presence of multiple components not present in the original extract. Band 2 (one of the major components recovered from the TLC) on GC-MS analysis showed the presence of one compound m/z 248 which was not present in the original methylene chloride extract. Band 4 on GC-MS analysis revealed the presence of two closely related structures: the isomerized starting material and naphthol. The use of preparative Gas Chromatography will be implemented to ensure a clean quantitative analysis of the pretreatment extracts and unequivocal identification of the major components.

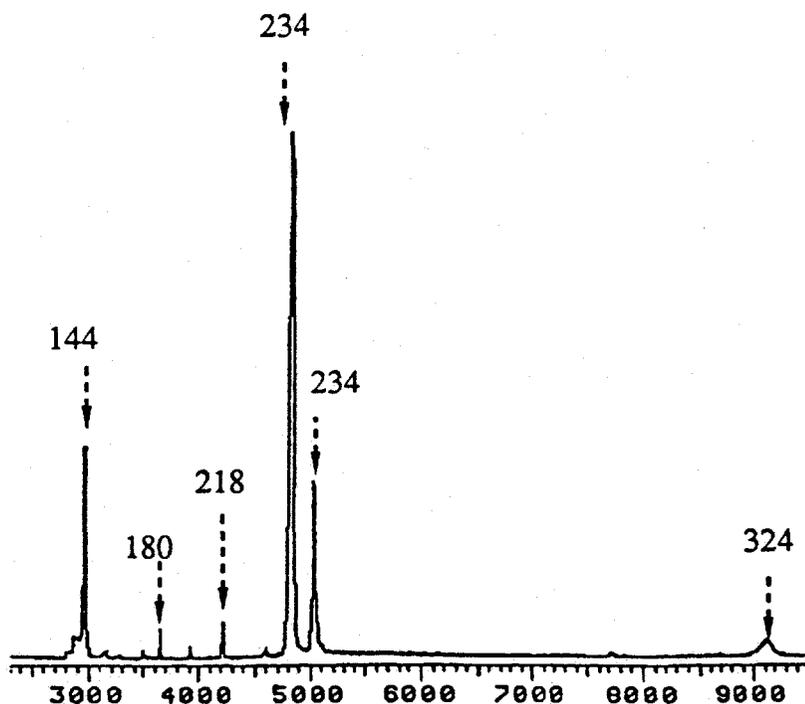
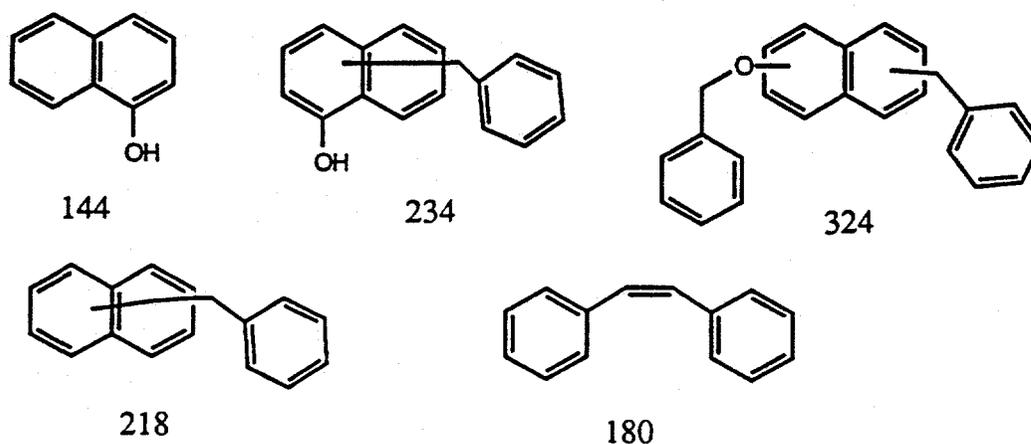


Figure 5. Steam pretreatment of α -BNE. GC-MS ion chromatogram (CI mode) of the methylene chloride extract showing the corresponding molecular weights.

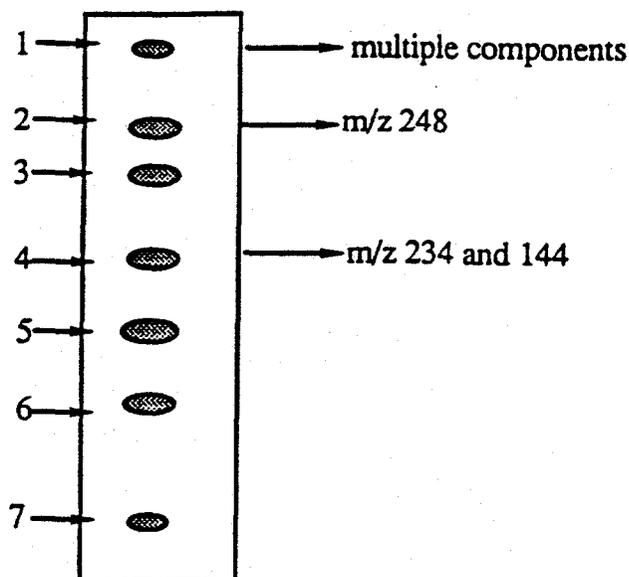


Figure 6. Steam pretreatment of α -BNE. TLC profile of methylene chloride extract on alumina.

A second pretreatment test was carried out using 100 mg of β -naphthylmethyl phenyl ether. Only 20 mg of extractable material was obtained with methylene chloride and none with pyridine. Evidently, there was an escape of material either because of pressure fluctuations encountered during this run or because of an undetected leak. This run is discarded.

WORK PLANNED FOR NEXT QUARTER

Installation of the autoclave will continue next quarter. Steam pretreatment experiments using a mixture of Illinois No.6 and Blind Canyon coal samples will be carried out next month. Identification of the major compounds from the methylene chloride extract of the steam pretreated α -benzyl naphthyl ether will be further refined and a mass balance constructed. The purification of model compound α -naphthylmethyl phenyl ether will be completed.

REFERENCES

1. Maa, P.S.; Neavel, R.C.; Vernon, L.W., 1984, Ind. Eng. Chem. Process Des. Dev., 23, 242-250.